PART TITLE: WVDP WASTE FORM QUALIFICATION REPORT - CANISTERED WASTE FORM SPECIFICATIONS

ITEM TITLE: SPECIFICATION FOR REMOVABLE RADIOACTIVE CONTAMINATION ON EXTERNAL SURFACES

3.7 Specification for Removable Contamination on External Surfaces[1]*

The level of non-fixed (removable) radioactive contamination on the exterior surface of each canistered waste form may be determined by wiping an area of 300cm^2 of the surface concerned with an absorbent material, using moderate pressure, and measuring the activity on the wiping material. At the time of shipment, the non-fixed radioactive contamination on the wiping mateial shall not exceed 22,000 dpm/100cm^2 of canister surface wiped for beta and gamma emitting radionuclides and 2,200 dpm/100cm^2 of canister surface wiped for alpha emitting radionuclides. Sufficient measurements shall be taken in the most appropriate locations to yield a representative assessment of non-fixed contamination levels.

In addition, the producer shall visually inspect each canistered waste form and remove visible waste glass from the exterior before shipment.

The producer shall describe the method of compliance in the WCP. The Producer shall provide the non-fixed radioactive contamination level results in the Storage and Shipping Records.

<u>WVDP COMPLIANCE STRATEGY</u>

The canistered waste form will be decontaminated with a nitric acid and Ce^{+4} solution. The WVDP will smear survey the canister's external surfaces according to 10 CFR 71.87(i) before shipout to the repository. The external surfaces of the canistered waste forms will also be visually inspected for visible glass, and if present, the glass will be removed.

<u>IMPLEMENTATION</u>

During production at WVDP, it is possible for the exterior surface of the WVDP canister to become radioactively contaminated due to the condensation and deposition of radionuclides from the atmosphere of the Vitrification Cell. Although simple washing could conceivably remove loosely adhering particles and films, a more effective technique is needed to rid the canister surface of strongly adhering and/or bonded contaminants. The most persistently bonded contamination would accrue when the canister is at elevated temperatures, due to its being filled with molten glass, and airborne radioactive compounds become incorporated into the oxidation (i.e., tarnish) layer that forms on the hot stainless steel canister. In order to remove this tenacious contamination, WVDP's strategy is to chemically mill off a thin layer of canister metal with its overlying oxide scale (that contains the radioactive compounds) thereby insuring a "clean canister surface" that is in compliance with the removable

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* The specification as provided in Reference (1) is reproduced here in boldface print.

(non-fixed) contamination limits of this specification at the time the canister is transferred to the on-site HLW Interim Storage Facility. Before shipout, each canister will be inspected, washed, and brushed to remove any loosely adhering contamination acquired while in storage and then smear tested to confirm that the canister surface is in compliance at the time of shipment.

Overview of the WVDP Decontamination Process

The WVDP reference decontamination process utilizes highly oxidizing Ce^{+4} ions dissolved in a dilute ~1M HNO_3 aqueous solution to chemically mill a thin metal layer from the canister surface. The decontamination reaction is achieved by immersing the canister in the 65°C decontamination solution (contained in an inert titanium tank) for about 6 hours while agitating the solution using a gentle air sparge*. The thickness of the stainless steel that is removed is limited to about 10 micrometers by the amount of Ce^{+4} available in solution; longer exposure times or higher temperatures will not increase the extent of the reaction. The decontaminated canister is then washed, first with dilute nitric acid and then water, air dried, and finally smear surveyed. The spent solution from the decontamination process is transferred to a hold tank and chemically treated with hydrogen peroxide to reduce any unreacted Ce^{+4} to the non-corrosive Ce^{+3} valence state. The resulting deactivated solution is then recycled into the vitrification process streams and finally becomes incorporated into subsequent batches of the vitrified waste form.

The reference WVDP chemical milling process was conceived and developed at Battelle Pacific Northwest National Laboratories and its efficacy demonstrated using small stainless steel coupons. In an early study[2], it was established that the extent of chemical milling, as measured by weight loss, increased with increasing Ce^{+4} concentration and that three moles of Ce^{+4} are required to dissolve one mole of iron** from the surface of the stainless steel, i.e.,

$$3Ce^{+4} \quad + \quad Fe^{0} \quad == \quad 3Ce^{+3} \quad + \quad Fe^{+3}$$

Since the reaction proceeds to completion, it was demonstrated that the amount of canister surface removal could be controlled simply by altering the concentration of Ce^{+4}. For example, about 1.4 moles of Ce^{+4} in a dilute nitric acid solution (~1M) will remove about 3 micrometers from 1 square meter of stainless steel while 2.3 moles of Ce^{+4} will remove about 5 micrometers. Other studies established the reaction kinetics and found that contact times of about 3 hours at temperatures above 65°C were more than adequate to achieve nearly complete (>90%) reaction. Further tests with non-oxidized stainless steel coupons, with oxidized coupons that were heat treated to simulate the

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* Note that in the elapsed time of about 8 days between filling the canister and transferring it to the decontamination station, the WVDP production canister surface temperature will be below 65°C.

** Ce^{+4} also reacts rapidly with the Ni and Cr components of the stainless steel forming soluble Ni^{+2} and Cr^{+3} ions. The presence of a heat tarnished oxide scale (due to thermal excursions from filling the canister with molten glass) has not been found to markedly affect the kinetics or efficiency of metal removal from the surface of stainless steel.

surface condition of heat tarnished production canisters and with radioactively contaminated non-oxidized and oxidized coupons revealed the following[2,3]:

- non-oxidized but radioactive coupons can be effectively decontaminated (to levels below this specification) by removing about 3 micrometers of stainless steel using Ce^{+4}.

- oxidized and radioactive coupons (which simulate production canister conditions) require the removal of 2.5 to 5 micrometers of stainless steel to be decontaminated with Ce^{+4}[3].

- nitric acid by itself is insufficient to produce effective decontamination.

- the reaction kinetics for Ce^{+4} milling of oxidized stainless steel is the same as for unoxidized stainless steel.

- stress corrosion cracking is not promoted by the Ce^{+4} process, even when a surface is extensively milled to remove up to 15 micrometers of stainless steel[4].

- no preferential attack of the 308L SS weld/label alloy vis-a-vis the 304L canister body alloy was observed[4].

- the decontamination solution can be deactivated with hydrogen peroxide according to the equation:

$$2Ce^{+4} + H_2O_2 == 2Ce^{+3} + 2H^+ + O_2$$

Full Scale Canister Testing[5]

Although laboratory tests provided proof of principle process data, additional experiments on surface oxidized full sized WVNS canisters with oxidized surfaces were performed to verify the operating parameters and to demonstrate the effectiveness of the process when scaled up by a factor of 5000X compared to laboratory tests. Other objectives of these experiments were to evaluate the uniformity of material removal as a function of location on the canister surface and to assess the extent of the problem of a residual oxide film or brown colored skin (i.e., onion skin) that was occasionally observed in laboratory tests to loosely adhere to the surface of the stainless steel after removing the coupons from the test solution (chemical milling) and drying.

The test equipment for these tests was designed and fabricated to match that used at the full scale WVDP canister decontamination station (described in the next section of this report). The eight full sized canisters used in these tests were originally filled with molten nonradioactive glass during the FACTS tests (1984-1989) at WVDP and therefore had an external oxide layer similar to that expected during actual production. Prior to the decontamination treatment, these canisters which had been stored on an outdoor hardstand, were washed to remove debris and dirt. In addition to immersion testing the full sized canisters, six preweighed test coupons that were cut from the walls of other filled and oxidized canisters, were affixed with silicone adhesive to various preassigned locations on the surface of the canisters; these locations included the sides of the canister at four longitudinal positions, the top shoulder and the center of the bottom dished head. The changes in weight of the coupons after the decontamination test provided the measure of the extent (depth) and uniformity of material milling by this Ce^{+4} process. The degree of cleanliness of the full sized canisters, as determined by the absence of the oxide tarnish layer and the absence of the onion skin, was used to gauge the effectiveness of the decontamination process.

The results of these full scale canister tests were consistent with earlier laboratory scale findings and provided support for the viability of this process for decontaminating production canisters; in addition, these tests provided guidance for improving and modifying process procedures and canister finish to help assure a more effective decontamination treatment. It was found that:

a) the extent of reaction averaged over 90% of theoretical, in agreement with laboratory studies.

b) the variability in the extent of milling or surface loss, as a function of location on the canisters, was less than 1 micrometer and could be minimized by increasing air flow to the sparge ring at the bottom of the decontamination tank to 5 SCFM.

c) the oxide tarnish layer on the canisters were removed from all surfaces, except from the bottom head. Incomplete cleaning of the bottom head was related to the relatively rough surface finish of the original head. The new WVNS canister equipment specification requires that both heads of the canister have the same surface finish as the rest of the canister, i.e., 63 rms.

d) chemical analysis of the Cr, Fe and Ni content in the spent decontamination solution are in agreement with calculations of material loss as measured by coupon weight changes.

e) patches of onion skin discoloration ($<250\ cm^2$) were randomly found on some decontaminated canisters, but these were readily removed by increasing the average targeted depth of material removal to about 5 micrometers and by spray washing the canister first with dilute $\geq 0.5M$ nitric acid followed by a water spray wash.

On the basis of these experiments as well as earlier laboratory tests, the process conditions that will be targeted for decontaminating production canisters are deliberately selected to be conservative so as to mill an excess thickness of metal thereby insuring complete removal of the oxidized tarnish layer and its accompanying radioactive contaminants. The decontamination conditions are approximately as follows: milling depth = 10 micrometers, temperature = 65°C, soak time = 6 hours, decontamination solution = about 550 liters containing 6.8 gm/liter Ce^{+4} (ceric nitrate) in ~1.0M HNO_3, air sparge rate = 5 SCFM. During production, the tolerances on these parameters will be less than ± 10%.

WVDP Canister Decontamination System

The function of the Canister Decontamination System is to remove radioactive contamination from the surface of the production canister and to recycle the removed contamination for reprocessing through the melter. An additional part of this system provides for swipe testing in order to furnish a general measure of the extent of canister decontamination. However, swipe testing results obtained during production will not, by themselves, be used as a criteria for measuring the success of the decontamination process. This follows because with increasing production time, the background contamination levels in the Vitrification Cell is expected to increase and in the worst case, could conceivably exceed the WAPS requirements for canister surface cleanliness. Therefore, the WVDP strategy will be to chemically mill 10 micrometers off the canister, a large quantity of metal amounting to a factor of two to three times more stainless steel than that experimentally found to be sufficient to remove the contamination/tarnish layer from a canister. This approach provides assurance that contaminants contained in the tarnish (oxide) layer have been removed from the canister surface even if the swipe survey results are inconclusive. Such extensive in-cell decontamination is expected to minimize the final cleaning efforts that will be necessary when the canisters are prepared for future shipment to the federal repository (i.e., when they must meet the WAPS contamination requirements as determined by swipe survey).

The WVDP Canister Decontamination System includes all vessels, piping, valves, and associated equipment required to prepare canister decontamination solutions, to transfer the decontamination solutions into the Vitrification Cell, to decontaminate the outside surface of canisters filled with vitrified high-level radioactive waste, to swipe the canister to confirm that decontamination has been satisfactorily accomplished, to neutralize the residual chemical milling capability of the decontamination solution by reducing the Ce^{+4} to Ce^{+3} thereby preventing corrosion of down-stream components, and to recycle the radiologically contaminated spent decontamination solutions back into the vitrification process.

The Canister Decontamination System, as diagrammed in Figure 1, consists of two stations, a decontamination station located inside the Vitrification Cell on the east wall at ground level, and a mixing station located ex-cell on the opposite side of the same wall on the third floor where the fresh, non-radioactive decontamination solution is prepared. The vertical separation facilitates gravity feed for the process chemicals from the mixing station to the decontamination station.

The decontamination station is located in front of a shield window. Auxiliary equipment includes a utility plug for transferring the decontamination chemicals from the mix station through the vitrification cell wall to the decontamination station. A transfer drawer is available for insertion and removal of swipes. A set of master slave manipulators (MSMs), and the overhead bridge cranes inside the Vitrification Cell are employed when performing canister decontamination operations.

As shown in Figure 1, the principle components of the in-cell decontamination station are the Canister Decontamination Tank (A) and the Neutralizer Tank (B). Both of these tanks are constructed of titanium, a material which is resistant to reaction with the Ce^{+4} solution. The Canister Decontamination Tank (A) is designed to receive the oxidized canister and the fresh decontamination solution. It contains a nozzle for decontamination solution addition, a sparge ring for solution agitation, a level probe, a thermowell to support temperature control, a heating/cooling coil to maintain the decontamination solution at the targeted 65°C reaction temperature and an upper spray ring for washing the outside surface of the decontaminated canister of spent solution/reaction product residues as it is withdrawn from the tank. The Neutralizer Tank (B) accepts the depleted solution from the Decontamination Tank as well as the wash(rinse) solutions and is where small (e.g., liter) quantities of H_2O_2 are added to deactivate the reactive Ce^{+4} ions to the inactive Ce^{+3} form. Deactivation or neutralization is necessary so that the stainless steel waste header and other downstream metal components are not attacked or compromised as the decontamination solution (i.e. the spent solution) is being recycled into the slurry feed makeup system. The Neutralizer Tank contains a nozzle for transfer of the waste Ce^{+4} solution, an inlet nozzle for deactivating the hydrogen peroxide solution, a vent to the vessel vent header, a sampling nozzle, a level probe and a sparge ring.

The ex-cell Mix Station equipment includes a nitric acid Holding Tank (C) and a ceric nitrate solution Charge Container (D), as shown in Figure 1. The Nitric Acid Holding Tank is equipped with service piping for water and nitric acid, remote level detection and a sight glass for visual level detection. From the tank to the wall penetration is a 2" titanium feed line with a penetration that accepts a line from the ceric nitrate Charge Container. This latter tank is designed for manual filling ceric nitrate to predetermined levels. In operation, a predetermined quantity of dilute (i.e., ~1M) nitric acid and ceric nitrate are added to the Holding Tank and to the Charge container, respectively. The quantity of each component is visually verified and then both the nitric acid and Ce^{+4} solutions are simultaneously released into the feed line where they become uniformly mixed while being transferred by gravity to the decontamination tank at the Decontamination Station. All transfer lines and components carrying the fresh Ce^{+4} solution from the Mix Station to and between the tanks in the Decontamination Station are made of titanium or non-reacting polymers.

Flow Path for Decontaminating WVDP Production Canisters

The process of canister decontamination starts at the weld station where visual and CCTV examinations for the presence of visible glass on the upper surface, the flange and the lid counterbore of the canister is performed. In the unlikely event that any adhering glass is found in these locations, a wire brush (see WQR 2.2, Canister Fabrication and Closure), a needle gun (to be discussed in a later section of this report) or other mechanical tool is used to dislodge the glass. After the closure lid has been successfully welded to the canister flange, the canister is grappled and transferred to the in-cell Decontamination Station where the following operations take place:

- Inspect canister for the presence of visible glass; if present, physically remove glass.
- Open lid on the canister decontamination tank, lower canister into the empty tank and replace the lid.

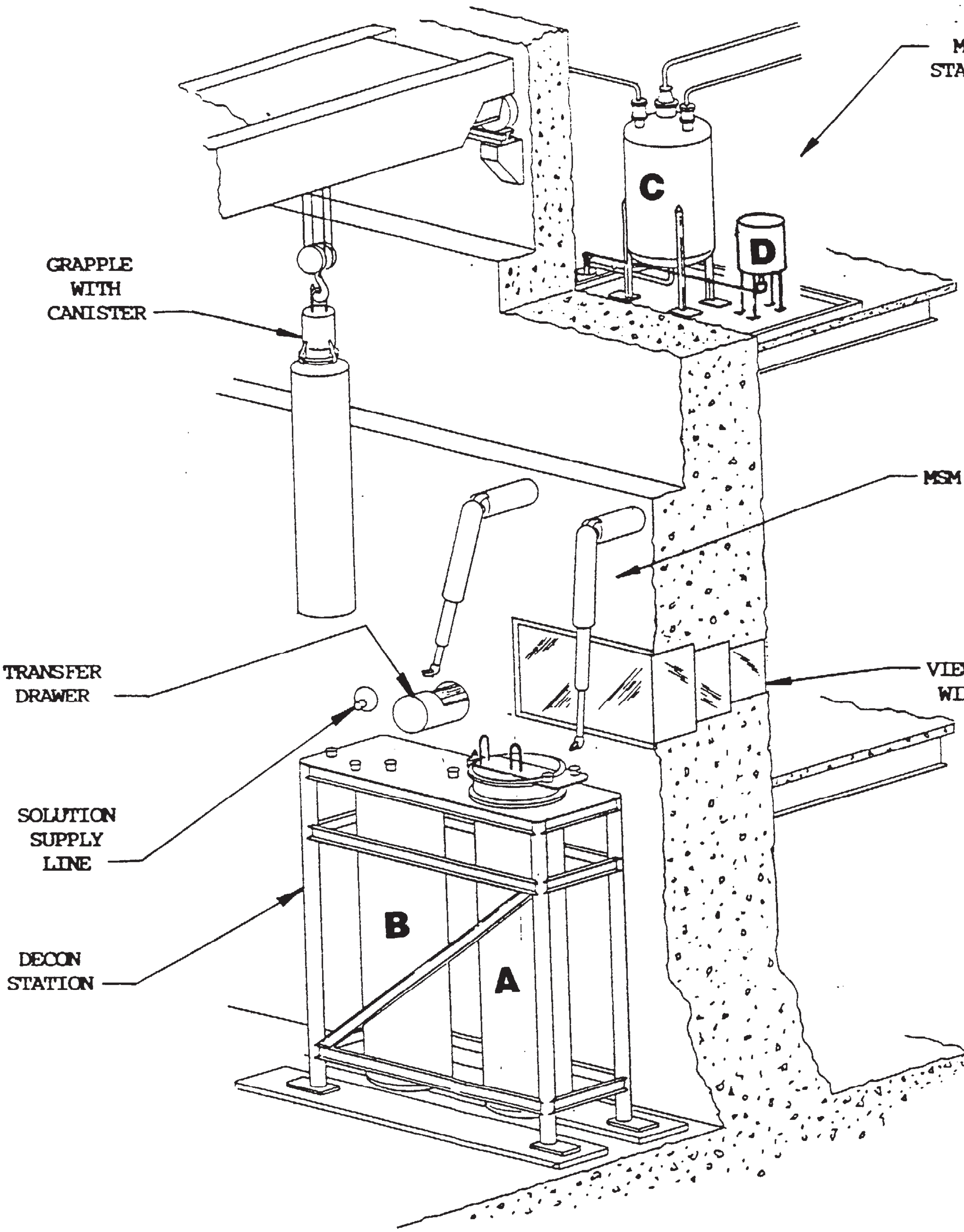

Figure 1. Schematic of the WVDP Ce+4 Canister Decontamination System

- Establish sparge air flow of 5 SCFM in the decontamination tank and accept transfer of approximately 540 liters of decontamination solution (~1M HNO_3 and ceric nitrate) from the mix station. The quantity of ceric nitrate in solution and therefore the depth of chemical milling of the canister surface will be targeted at 10 micrometers of stainless steel.

- Adjust the temperature of the decontamination solution to 65°C (via heating/cooling coils) and maintain temperature for 6 hours.

- Transfer spent decontamination solution to the Neutralizer Tank.

- Remove Decontamination Tank lid and grapple the canister.

- Initiate 0.9M HNO_3 spray wash flow (to remove solution residue from the canister) and lift the canister through the spray rings. When the canister is clear of the spray rings, shut off spray.* Transfer acid rinse to the Neutralizer Tank. Lower canister back into the Decontamination Tank.

- Transfer wash (rinse) solutions from Decontamination Tank to the Neutralizer Tank, add hydrogen peroxide to deactivate the spent decontamination and wash solutions and transfer contents to the downstream slurry feed make-up system. Repeat spray wash procedure using water. (Note: Return canister to the now empty Decontamination Tank to dry. The water wash is returned to the tank farm.)

- Swipe the air dried canister according to the plan described in the next section of this report. The three locations are under the flange, on the side walls and the bottom head.

- Transfer cleaned (decontaminated) canister to the HLW Interim Storage Facility and place into storage rack. Before shipout, wash/brush loosely adhering contamination from the canister, inspect for surface glass and remove if present (with needle gun) and perform smear survey.

Canister Smear Procedure/Equipment

WVDP will comply with this specification by smear testing each canister in accordance with the procedure in 10 CFR 71.87(i) to determine the amount of non-fixed radioactive surface contamination. These tests will be performed at the decontamination station after the Ce^{+4} chemical milling step but before the canister is transferred to the interim storage facility. A final smear test will be performed in the loadout (shipping) facility prior to shipout of the canister. The in-cell smear test involves remotely wiping a 1.75 inch (4.45 cm) diameter cloth smear pad against the surface of a canister while the canister is suspended by the grapple and positioned in front of the shield window. The plan is to perform 6 smears on each canister where each smear will

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* As the canister is raised through the spray rings, it will again be inspected on all surfaces for the presence of visible glass. If present, the glass will be physically removed and the canister will be decontaminated again.

cover about a 550 cm^2 area. Smearing will be done under the lifting flange (covering about two 120° segments), along the entire length of the canister body at two diametrically opposed positions**, and along an arc on the bearing surface (i.e., high spot) of the bottom head of the canister (covering about two 120° segments).

The WVDP Swipe Assembly is shown in Figure 2. This assembly consists of three component parts; the handle, the foam swipe section and the cover. The handle consists of a round base and a square body for handling with MSMs; it can be used for multiple swipe operations. The foam swipe section consists of a round disc base attached to a closed cell compressible foamed polymer cylinder. Attached to the end of the foam cylinder is a removable adhesive backed cloth smear pad of the same diameter. Plastic foam is used on the swipe section to provide a visual indication of compression and allow for continuous contact with the canister. The cover is used to protect the swipe section (pad) from additional contamination while being handled and transported into and out of the Vitrification Cell. The handle and swipe sections are attached together with a breakaway adhesive backed Velcro™ system. The Velcro™ allows the swipe section and cover to be separated from the handle which can become contaminated from contact with the manipulator fingers. The detached swipe section and cover may then be safely transferred out of the cell through the transfer drawer for count analysis.

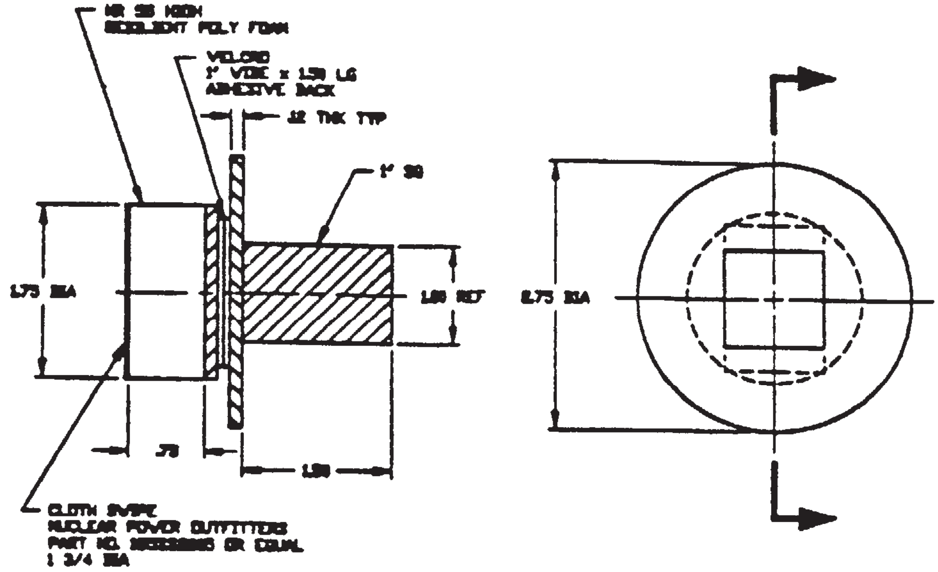
When smear testing a canister during production, six foam swipe sections with attached covers and one handle will be transferred, via the transfer drawer, into the Vitrification Cell. After completing the swipes on the canister, the six swipe sections with covers will be transported ex-cell through the transfer drawer into a glove box where they will be monitored for radiation dose rate, and packaged and transported to the laboratory. At the laboratory, the covers will be removed, and the smear pads will be peeled from the foam cylinders and counted using standard alpha and beta/gamma proportional counters. The results from each canister, prior to storage, will be recorded in the WVDP internal process log.

Before shipout, additional smears will be taken and the smear results, which will be traceable to each labeled canistered waste form, will be reported in the Storage and Shipping Records. If any smear test result exceeds the specified limit, the canister will be decontaminated and smeared again on all surfaces.

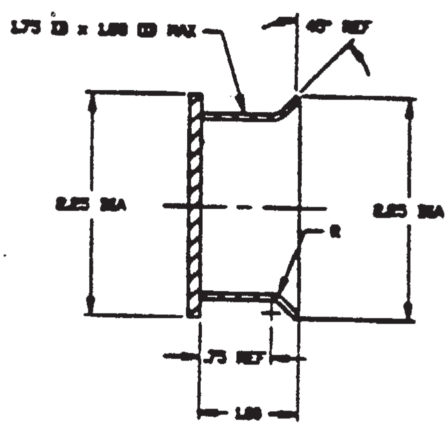
Visible Glass Removal

Visual inspection of the canisters, either by direct observation through the shield windows or via closed circuit television cameras, will be made before transfer to interim storage to assure that no waste glass is adhering to the canister. Glass deposits should be readily visible, especially after canister decontamination, because of the large differences in reflectivity and color between the glass and the stainless steel canister. Since the etched, decontaminated canister is a silvery gray matte color[5], it is unlikely that any sizable thickness of black nuclear waste glass would not be visible against this background. The results of the surface inspection will be recorded in the WVDP internal process log. If glass is found to be adhering to the

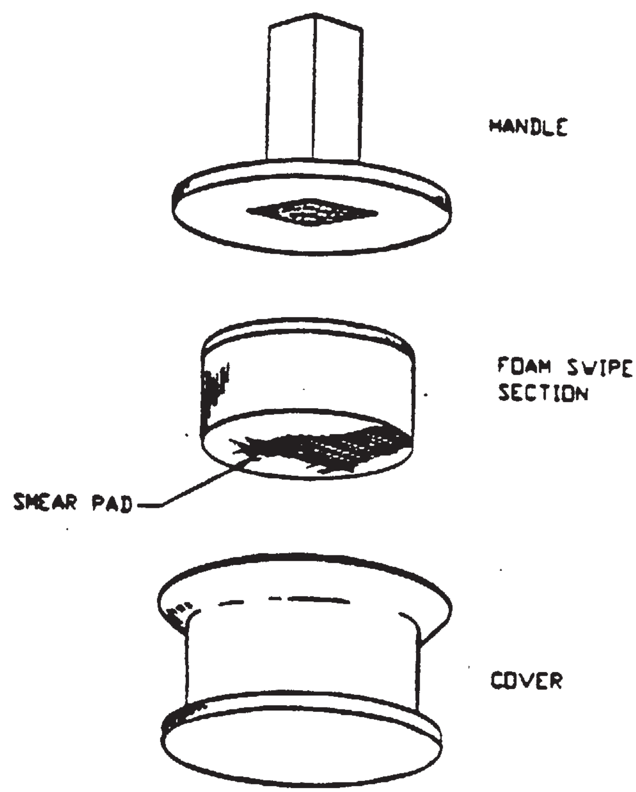
** Note - the longitudinal swipes will be performed by positioning the smear pads against the side of the canister for a predetermined time as the canister is lifted at a constant rate with the crane.



SWIPE ASSEMBLY



COVER



EXPLODED VIEW

Figure 2. Schematic Design of the WVDP Canister Swipe Assembly
(Dimensions in inches)

canister before or after decontamination, it will be removed by means of a pneumatic needle gun or other suitable device. After removal of the glass, the canister will again be decontaminated in the Ce^{+4} solution. As a result of this treatment, it is expected that the surface contamination will be removed along with the evidence as to where the glass originally was. This twice decontaminated canister will then be treated as any other canister. WVNS has had hands-on experience in glass removal when a pour incident during FACTS testing resulted in the accumulation of a layer of glass on the top flange and side wall of a canister. Attempts at chiseling the glass off the surfaces proved to be unsuccessful but a pneumatic powered needle gun was demonstrated to be very effective in removing the tightly adhering glass. Accordingly, in production, WVDP will have at standby a needle gun and holder assembly (or other mechanical device) that can be remotely manipulated by MSMs to remove visible glass from its canisters. The details of this equipment have been described in DWPF's Waste Form Qualification Report[6].

DOCUMENTATION

Smear tests and a visual inspection of each canister will be performed in the WVDP shipout facility. These smear test results and a verification that no visible glass remains on the surface of each canister will be provided in the Storage and Shipping Records.

REFERENCES

†1. Waste Form Compliance Plan for the West Valley Demonstration Project High Level Waste Form, WVDP-185, Rev. 11, 1996.

†2. WVNS-DP-028, Rev. 0, 1996, "Development of Ce(IV) Decontamination Process," West Valley Demonstration Project, West Valley, NY.

†3. WVNS-DP-021, Rev. 1, 1996, "Ce^{+4} Decontamination Testing of Stainless Steel Coupons," West Valley Demonstration Project, West Valley, NY.

†4. WVNS-DP-008, Rev. 1, 1996, "Canister Weld Bead Legibility Following Decontamination," West Valley Demonstration Project, West Valley, NY.

†5. Studd, M.G., "Full Scale Canister Decontamination Test Report," WVNS-SR-010, Rev. 0, December 1994.

†6. DWPF Waste Form Qualification Report, Volume 11, Appendix 3, 1994.

† These references are required to demonstrate conformance with the WCP compliance strategy.

WVNS RECORD OF REVISION

DOCUMENT

If there are changes to the controlled document, the revision number increases by one. Indicate changes by one of the following:

- Placing a vertical black line in the margin adjacent to sentence or paragraph that was revised.
- Placing the words GENERAL REVISION at the beginning of the text.
- Placing either FC#> or PC#> (whichever applies) in the left-hand margin at the beginning of the paragraph or section where the field/page change has been made AND placing a vertical black line in the margin adjacent to the actual change.

Example:

The vertical line in the margin indicates a change. |

FC1> The FC#> in the margin along with the vertical line (redline) indicates a change. |

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	12/16/94
1	Revision made per Technical Review Group comments (reference letter CD:95:0025). Identification of key references.	2,3,4,6, 8,9,11	08/14/96
2	Update page numbering format.	All	02/06/97
	Corrected title of Pacific Northwest Laboratories (PNL) to Pacific Northwest National Laboratories (PNNL).	2	
	Revise decontamination process description to reflect vitrification production conditions.	2,3,4, 5,6,8,9, 11	
	Updated format of data package references for consistency and renumbered references in text as necessary.	11	
3	Update Specification 3.7 to correspond with the new EM-WAPS, Revision 2. Update swipe technique to reflect current practice (reference letter CD:97:0049).	1,8,9,11	09/05/97

WVNS RECORD OF REVISION CONTINUATION FORM

Rev. No.	Description of Changes	Revision On Page(s)	Dated